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Comment on "Photoselection in uniaxial liquid crystals: The effect of rotational Brownian motion on measurements of orientational distribution functions"

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Naqvi[1] in the above comment points to a nonphysical result reported in the theoretical section of the second of our recent papers[2,3] on the effect of rotational mobility on the fluorescent emission of probes embedded in oriented media (e.g., liquid crystals or membranes). In our previous articles, we have attempted to introduce in a simple manner the complications of rotational motion of a probe molecule during the lifetime of the fluorescence process and the possibility of nonparallelism of the absorption and emission dipoles. Our discussion illustrated the importance of these frequently neglected factors in the analysis of experimental data to obtain the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters in nonrandom systems.

In the limit where the fluorophores are essentially static, we derived an expression for the emission anisotropy (case where absorption oscillator is parallel to long axis of probe and emission oscillator is at an arbitrary angle δ) and showed how to extract $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from experimental data. Our treatment of the dynamics of the probe molecule was oversimplified as it was based upon the assumption of rotational diffusion under spherical symmetry (equivalent in concept of all of Naqvi's R_i being equal). That is, the time dependence of the angular probability distribution function was, in our discussion, governed by a free diffusion equation [Eq. (21) of Ref. 2]. The diffusion was subject however to a nonrandom initial boundary condition which reflected the uniaxial symmetry of the host environment. Because of this simplified (and unphysical) diffusion equation, the anisotropy of emission will vanish for long times, i.e. $r(\infty) = 0$ in the model. This aspect is contrary to physical intuition as the system would not relax to the equilibrium distribution characteristic of an ordered medium. Our results can therefore be considered correct only for short times (or $\tau/\tau_R \ll 1$). Fortunately this was shown to be the case in our experiments on the liquid crystal MBBA where the probe is highly hindered[3] and the conclusions of this paper are valid.

Szabo[4] has recently presented a general theoretical development that pertains to this problem. He has considered the effect of rotational motion of a fluorescent probe (of arbitrary oscillator geometry), describing the diffusion in a potential which is consistent with the equilibrium distribution expected for uniaxially oriented systems. Both the short and long time behavior of $r(t)$ is considered in this work. Szabo finds that the expression for a finite $r(\infty)$ [Eq. (31)] of our first article[2] is correct; although, as we have noted, the derivation of this particular equation is an error on our part.

[1] K. R. Naqvi, J. Chem. Phys. 73, 3019 (1980), preceding comment.
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[3] L. L. Chapoy and D. B. DuPré, J. Chem. Phys. 70, 2550 (1979).
[4] A. Szabo, J. Chem. Phys. 72, 4620 (1980).

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